Crystal Structure of Tetraphenylarsonium Tetranitratozincate(2−), and Optical Spectrum of Tetranitratocobaltate(2−)

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The title compound crystallises in a monoclinic cell of dimensions: a = 23.355(5), b = 11.334(5), c = 18.588(5) Å, β = 107.5(1)°, space group $C2/c$. The structure was determined from diffractometer data by the heavy-atom method and refined to R 0.069. Although the eight-co-ordinate $[Zn(NO_3)_4]^{2-}$ ion has approximately D_{2d} dodecahedral symmetry, there is a large difference between Zn–O bond lengths r_A and r_B (means 2.06 and 2.58 Å), indicating contributions by a resonance form of the molecule, also reflected in N–O bond lengths. Various explanations are given for these bond-length differences, but they probably reflect the tendency of zinc(II) to give tetrahedral co-ordination.

This complex was used as a diamagnetic matrix into which Co^{2+} was dissolved and the polarised optical spectra of the mixed crystals measured. An assignment for $[Co(NO_3)_4]^{2-}$ in D_{2d} symmetry is suggested, the sequence of components derived from parent T_d symmetry being: ${}^4T_1(F)$: ${}^4E > {}^4A_2$; ${}^4T_1(P)$: ${}^4E > {}^4A_2$, ground state ${}^4B_1$.

THE d-orbital energy-level orders in eight-co-ordinate environments of dodecahedral symmetry have aroused recent interest and several crystal field [1] and angular overlap [2] calculations which attempt to rationalise the e.s.r. and electronic spectra of $[CuO_8]$ chromophores have been reported.[3] Although one of the first transition-metal complexes proved to have this stereochemistry, $[Co(NO_3)_4]^{2-}$ (ref. 4) has been investigated only cursorily.[4,5] We report the polarised electronic spectra of single crystals containing this species, both in a pure complex and diluted in the Zn^{II} analogue, together with the crystal structure of the diamagnetic matrix $[AsPh_4]_2[Zn(NO_3)_4]$ which was determined from diffractometer data.

EXPERIMENTAL

$[AsPh_4]_2[Zn(NO_3)_4]$ and its Co^{II} analogue were prepared by literature methods,[3] all manipulations being carried out in a dry-box with freshly distilled solvents. The cobalt complex itself could be induced to give only small, though well-formed, crystals on slow recrystallisation from chloroform. To obtain larger crystals, the cobalt complex was diluted into the zinc analogue by allowing CCl_4 to diffuse very slowly into a chloroform solution of the components. This procedure gave crystals sufficiently large to permit measurement of spectra in more than one crystal face and also for us to obtain spectra of the near-i.r. region. Nominal concentrations of 10% dopant were used; these differed only in absolute intensities from samples containing 5 or 15% Co^{2+}.

Optical spectra were measured on a Shimadzu MPS 50L spectrophotometer, having a single polariser (220—800 nm), and, for larger crystals, on a Beckmann DK 1A spectrophotometer equipped with a pair of Glan–Thompson polarisers (800—2 500 nm). Spectra were obtained from freshly prepared crystals and crystallographic axes were identified by X-ray methods.

Crystal Data for $[AsPh_4]_2[Zn(NO_3)_4]$.—$C_{48}H_{40}As_2N_4O_{12}Zn$, M = 1 079.8, Monoclinic, a = 23.355(5), b = 11.334(5), c = 18.588(5) Å, β = 107.5(1)°, D_c = 1.53, Z = 4, F(000) = 2 194.28. Space group $C2/c$ or Cc from systematic absences: $h0l$ odd and hkl for h and k odd; shown to be $C2/c$ (No. 15) by successful refinement of the structure. Mo-K_α radiation, λ = 0.7107 Å; μ(Mo-K_α) = 20 cm^{-1}.

Accurate cell parameters were obtained by a least-squares refinement of 24 reflections from a crystal centred on a Philips Pailred P 1100 diffractometer by use of Zr-filtered Mo-K_α radiation. The preliminary data of ref. 6 are essentially confirmed.

Intensity Data and Refinement of the Structure.—Intensities were collected on the P 1100 diffractometer by use of Zr-filtered Mo-K_α radiation and the θ—2θ scan technique. The crystal was coated with lacquer to avoid decomposition in air. There was no evidence of deterioration of the crystal during data collection. 5 080 Independent reflections were collected, of which 3 236 with $I \geqslant 3\sigma(I)$ were used for structure refinement. Corrections were made for background count, Lorentz and polarisation effects but not for absorption.

Since we confirm that the zinc complex is isomorphous with the manganese analogue,[6] a structure-factor calculation was carried out with the atomic co-ordinates of the latter, and gave R 0.20. Four cycles of block-diagonal least-squares with isotropic thermal parameters for all atoms gave R 0.11. Four further cycles of refinement were then carried out with anisotropic thermal parameters for the $[Zn(NO_3)_4]^{2-}$ unit and for the arsenic atom but isotropic thermal parameters for the carbon atoms of the phenyl groups and this gave R 0.069. A further cycle of refinement indicated no shifts in atomic positions and thermal parameters $> 3\sigma$.

The quantity minimised in the least-squares analysis was $R' = \Sigma w(k|F_o| - |F_c|)^2$ where $w = [a + bkF_o + c(kF_o)^2]^{-1}$, with a = 4.0, b = 1.0, and c = 0.005.

The atomic scattering factors of ref. 7 for zinc, arsenic, oxygen, and nitrogen were used, the first two being corrected for the real component of anomalous dispersion.[8] Calculations were carried out on the Univac 1110 computer of Rome University with programs of ref. 9.

RESULTS AND DISCUSSION

Crystal Structure of $[AsPh_4]_2[Zn(NO_3)_4]$.—Final atomic positional parameters and anisotropic thermal parameters for $[Zn(NO_3)_4]^{2-}$ and the arsenic atom, together

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[1] See *e.g.* C. D. Garner and F. E. Mabbs, *J. Chem. Soc.* (*A*), 1970, 1711.

[2] D. W. Smith, *J. Chem. Soc.* (*A*), 1971, 1209.

[3] D. E. Billing, B. J. Hathaway, and P. Nichols, *J. Chem. Soc.* (*A*), 1970, 1877.

[4] D. K. Straub, R. S. Drago, and J. T. Donoghue, *Inorg. Chem.*, 1962, **1**, 848.

[5] J. G. Bergman and F. A. Cotton, *Inorg. Chem.*, 1966, **5**, 1208.

[6] J. Drummond and J. S. Wood, *J. Chem. Soc.* (*A*), 1970, 226.

[7] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[8] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[9] J. R. Carruthers and R. Spagna, unpublished work.

with estimated standard deviations, are listed in Table 1. Observed and calculated structure amplitudes are contained in Supplementary Publication No. SUP 21616 (12 pp., 1 microfiche).* Bond distances and angles for the molecule are shown in Table 2.

TABLE 1

Positional (× 10^4) and thermal parameters, with estimated standard deviations in parentheses

Atom	x	y	z	B/Å^2
Zn	5 000	8 342	2 500	
O(1)	5 558(3)	9 577(6)	2 267(5)	
O(2)	5 995(5)	7 985(7)	2 273(6)	
O(3)	6 403(4)	9 538(8)	2 032(5)	
N(1)	6 012(4)	9 035(7)	2 203(5)	*
O(4)	5 333(4)	7 037(6)	3 296(7)	
O(5)	5 637(6)	8 592(8)	3 926(7)	
O(6)	5 810(4)	6 921(8)	4 454(5)	
N(2)	5 614(4)	7 536(8)	3 924(5)	
As	8 401(0)	8 083(1)	1 515(1)	
C(11)	8 864(3)	7 615(6)	871(5)	3.55(12)
C(12)	8 750(3)	8 101(6)	168(5)	4.27(14)
C(13)	9 047(4)	7 619(8)	−334(6)	5.34(18)
C(14)	9 444(4)	6 696(8)	−96(6)	5.57(19)
C(15)	9 561(4)	6 268(8)	611(5)	4.97(17)
C(16)	9 274(4)	6 693(7)	1 129(5)	4.55(15)
C(21)	8 905(3)	8 367(5)	2 523(4)	3.22(11)
C(22)	9 256(4)	9 376(7)	2 691(5)	4.73(16)
C(23)	9 582(4)	9 614(7)	3 454(5)	4.96(16)
C(24)	9 547(4)	8 843(8)	4 016(5)	5.14(17)
C(25)	9 196(4)	7 824(7)	3 838(6)	4.80(16)
C(26)	8 879(3)	7 572(7)	3 088(5)	4.25(14)
C(31)	7 866(5)	6 824(6)	1 551(5)	3.65(12)
C(32)	7 472(4)	6 969(7)	1 976(6)	4.90(16)
C(33)	7 066(4)	6 032(8)	1 993(6)	5.48(18)
C(34)	7 084(4)	5 016(8)	1 586(6)	5.41(17)
C(35)	7 477(4)	4 899(8)	1 150(6)	5.66(18)
C(36)	7 879(3)	5 795(7)	1 128(5)	4.33(14)
C(41)	7 934(3)	9 463(6)	1 141(4)	3.34(11)
C(42)	8 217(4)	10 532(7)	1 119(5)	4.75(16)
C(43)	7 872(4)	11 549(8)	893(6)	5.54(19)
C(44)	7 242(4)	11 501(7)	690(5)	4.87(16)
C(45)	6 965(4)	10 412(7)	699(5)	4.91(16)
C(46)	7 306(3)	9 397(6)	935(5)	4.19(14)

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
As	17(0)	54(0)	28(0)	−5(0)	19(0)	3(1)
Zn	33(0)	72(1)	47(1)	0	39(1)	0
O(1)	41(2)	127(7)	93(5)	8(6)	74(6)	16(10)
O(2)	64(3)	139(8)	98(6)	10(8)	108(8)	14(11)
O(3)	42(2)	188(10)	89(5)	48(7)	81(6)	−30(11)
N(1)	36(2)	118(8)	62(5)	−25(7)	53(5)	−23(10)
O(4)	48(3)	133(8)	52(4)	−34(7)	21(5)	35(8)
O(5)	94(5)	122(8)	102(7)	−8(10)	90(9)	−56(12)
O(6)	57(3)	261(14)	41(4)	96(10)	45(5)	59(11)
N(2)	32(2)	153(9)	44(4)	20(7)	39(5)	1(10)

* Anisotropic thermal parameters (×10^4) of the form: $\exp(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)$, with standard deviations in parentheses.

Although the crystal structure of this complex was solved essentially in order to have a diamagnetic matrix of known crystal structure to aid interpretation of spectroscopic results, several aspects of the structure are of interest in themselves. First, the structure determination has allowed more accurate atomic positions to be found than was the case previously.[5,6]

The tetranitratozinc(II) unit is eight-co-ordinate dodecahedral (Figure 1). Table 3 lists equations of best mean planes through the two crystallographically independent nitrate ions [planes (3) and (4)] and the two trapezoidal planes of the dodecahedron [planes (1) and (2)]; the dihedral angle between planes (1) and (2) is

TABLE 2

Interatomic distances (Å) and bond angles (°), with standard deviations in parentheses

(*a*) $[Zn(NO_3)_4]^{2-}$

Zn–O(1)	2.046(8)	Zn–O(4)	2.071(7)
Zn–O(2)	2.516(12)	Zn–O(5)	2.636(11)
N(1)–O(1)	1.261(12)	N(2)–O(4)	1.287(11)
N(1)–O(2)	1.199(11)	N(2)–O(5)	1.199(13)
N(1)–O(3)	1.198(14)	N(2)–O(6)	1.181(12)
O(1)–Zn–O(2)	52.8(3)	O(4)–Zn–O(5)	51.8(3)
O(1)–N(1)–O(2)	114.7(10)	O(4)–N(2)–O(5)	116.8(9)
O(1)–N(1)–O(3)	121.5(9)	O(4)–N(2)–O(6)	117.5(9)
O(2)–N(1)–O(3)	123.6(11)	O(5)–N(2)–O(6)	125.6(10)

(*b*) $[AsPh_4]^+$

As-C(11)	1.913(9)	As–C(31)	1.911(7)
As–C(21)	1.917(7)	As–C(41)	1.913(6)
C(11)–C(12)	1.37(1)	C(21)–C(22)	1.39(1)
C(12)–C(13)	1.43(2)	C(22)–C(23)	1.42(1)
C(13)–C(14)	1.38(1)	C(23)–C(24)	1.38(1)
C(14)–C(15)	1.35(1)	C(24)–C(25)	1.40(1)
C(15)–C(16)	1.41(2)	C(25)–C(26)	1.40(1)
C(16)–C(11)	1.40(1)	C(26)–C(21)	1.40(1)
C(31)–C(32)	1.39(1)	C(41)–C(42)	1.39(1)
C(32)–C(33)	1.43(1)	C(42)–C(43)	1.40(1)
C(33)–C(34)	1.39(1)	C(43)–C(44)	1.41(1)
C(34)–C(35)	1.40(2)	C(44)–C(45)	1.40(1)
C(35)–C(36)	1.39(1)	C(45)–C(46)	1.39(1)
C(36)–C(31)	1.41(1)	C(46)–C(41)	1.40(1)
C(11)–As–C(21)	111.2(3)	C(41)–As–C(11)	111.5(3)
C(21)–As–C(31)	107.9(3)	C(11)–As–C(31)	108.3(3)
C(31)–As–C(41)	108.4(3)	C(21)–As–C(41)	109.4(3)
C(11)–C(12)–C(13)	118.5(7)	C(21)–C(22)–C(23)	119.0(8)
C(12)–C(13)–C(14)	119.5(9)	C(22)–C(23)–C(24)	119.9(8)
C(13)–C(14)–C(15)	120.3(10)	C(23)–C(24)–C(25)	120.5(8)
C(14)–C(15)–C(16)	122.9(8)	C(24)–C(25)–C(26)	120.2(9)
C(15)–C(16)–C(11)	115.8(8)	C(25)–C(26)–C(21)	119.2(7)
C(16)–C(11)–C(12)	123.0(8)	C(26)–C(21)–C(22)	121.2(7)
C(31)–C(32)–C(33)	118.8(8)	C(41)–C(42)–C(43)	119.5(7)
C(32)–C(33)–C(34)	118.4(10)	C(42)–C(43)–C(44)	120.8(8)
C(33)–C(34)–C(35)	121.7(9)	C(43)–C(44)–C(45)	118.8(8)
C(34)–C(35)–C(36)	120.9(9)	C(44)–C(45)–C(46)	120.8(7)
C(35)–C(36)–C(31)	117.3(9)	C(45)–C(46)–C(41)	119.6(7)
C(36)–C(31)–C(32)	122.9(7)	C(46)–C(41)–C(42)	120.4(6)

TABLE 3

Equations of mean planes in the form: $lx + my + nz = d$, where direction cosines are referred to an orthogonal axis system. Distances (Å) of atoms from planes are given in square brackets

	l	m	n	d
Plane (1): Zn, O(1), O(2), O(1)′, O(2)′	0.4787	0.0	0.8780	6.3328
Plane (2): Zn, O(4), O(5), O(4)′, O(5)′	−0.8450	0.0	0.5348	−8.8021
Plane (3): N(1), O(1)—(3) [N(1) −0.0243, O(1) 0.0075, O(2) 0.0081, O(3) 0.0087]	0.4779	0.1155	0.8708	7.4538
Plane (4): N(2), O(4)—(6) [N(2) 0.0101, O(4) −0.0030, O(5) −0.0035, O(6) −0.0036]	−0.8603	0.0555	0.5068	−8.5727

Dihedral angles (°) between planes:

(1)–(2) 86.3, (3)–(4) 87.9

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

86.3°, compared to an ideal value of 90° for the dodecahedron.[10]

The $[Zn(NO_3)_4]^{2-}$ unit is closer to C_{2v} than to D_{2d} symmetry, deviations of bond lengths from those of idealised D_{2d} symmetry ($\bar{4}2m$) being similar to those in the manganese analogue[6] and to those in the cobalt complex.[5] Thus, the two bond lengths Zn–O(1) and Zn–O(4) defining the A positions of the dodecahedron, r_A, are 2.046(8) and 2.071(7), respectively; Zn–O(2) and Zn–O(5), r_B, are significantly different, being 2.516(12) and 2.636(11) Å, respectively. As with the manganese analogue, these differences may be ascribed to packing forces in the crystal.

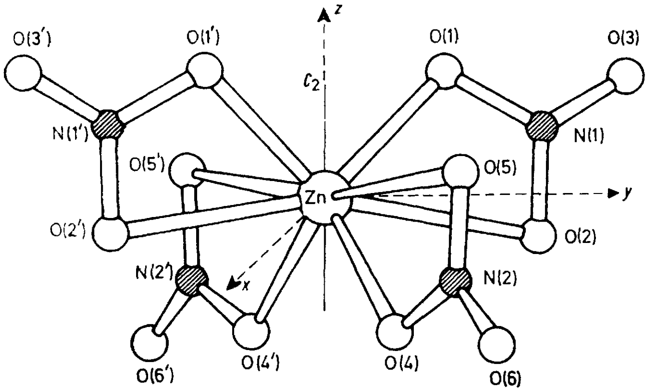

FIGURE 1 Co-ordination polyhedron for $[Zn(NO_3)_4]^{2-}$ showing the system of molecular axes (see text)

TABLE 4

(a) Dodecahedral shape parameters for $M(NO_3)_4$ species [a]

Parameter	Best polyhedron [b]	$Ti(NO_3)_4$ [c]	$[Fe(NO_3)_4]^-$ [d]	$[Mn(NO_3)_4]^{2-}$ [e]	$[Co(NO_3)_4]^{2-}$ [f]	$[Zn(NO_3)_4]^{2-}$ [g]	$Sn(NO_3)_4$ [h]
r_A/Å	2.06	2.07	2.13$_5$	2.27	2.07	2.06	2.17
r_B/Å	2.00	2.06		2.34	2.45	2.58	2.15
θ_A/°	35.2	37.0		43.0	46.5	46.8	38.9
θ_B/°	75.5	81.0		83.7	80.5	80.7	81.7
a/Å	2.34	2.51		3.09	2.99	2.94	2.73
m/Å	2.34	2.13		2.08	2.04	2.09$_5$	2.14
g/Å	2.48	2.73		3.15	3.02	3.14	2.88
b/Å	2.98	2.95		3.33	3.54	3.67	3.07

(b) Crystal data

Space group		$P2_1/c$	$P2_1/c$	$C2/c$	$C2/c$	$C2/c$	$P2_1/c$
a/Å		7.80(1)	13.412(10)	23.35(3)	23.47	23.355(5)	7.80(1)
b/Å		13.57(1)	13.963(10)	11.37(2)	11.34	11.334(5)	13.85(1)
c/Å		10.34(2)	21.667(15)	18.36(3)	18.57	18.588(5)	10.23(1)
β/°		125.0(2)	136.42(15)	107.0	107.0	107.5(1)	123.6(2)

[a] Distances are means. [b] Ref. 14. [c] Ref. 16. [d] Ref. 15. [e] Ref. 6. [f] Ref. 5. [g] This work. [h] Ref. 12.

The N–O distances in the manganese analogue are approximately the same. However, in the zinc complex these distances are very different from one another. Thus, N(1)–O(2) and N(2)–O(5) [both 1.199 Å] are shorter, and those involving the shorter Zn–O bonds [N(1)–O(1) and N(2)–O(4)] longer (mean 1.27 Å) than that in the free nitrate ion [1.245 Å (ref. 11)]. The terminal N–O bonds are similar to the former (mean 1.19 Å). These bond lengths are intermediate between those for uni- and for bi-dentate nitrato-groups,[12] which suggests that both resonance forms of the molecule

are important. Comparison may be made with $[Au(NO_3)_4]^-$, a planar structure with unidentate nitrato-groups, in which terminal N–O bonds are 1.23 and 1.17 Å (means), and that involving co-ordinated oxygen is 1.37 Å.[13]

In $[Zn(NO_3)_4]^{2-}$ the difference between mean r_A and r_B distances is large (0.52 Å), with r_A/r_B 0.80. This is greater than in the cobalt ($r_A - r_B$ 0.38 Å; r_A/r_B 0.84) and much greater than in the manganese analogue ($r_A - r_B$ 0.07 Å; r_A/r_B 0.97). Table 4 shows a comparison of shape parameters[14] for dodecahedral tetranitrato-complexes, and shows that the zinc complex is in many ways the most distorted (while still remaining dodecahedral).

There have been several attempts to explain differences between r_A and r_B in dodecahedral complexes. The observation that $r_A < r_B$ in $[Co(NO_3)_4]^{2-}$ was ascribed to the differing *d* electron–ligand repulsions between ligand atoms close to the *xy* plane (B sites) and those close to the $d_{xz,yz}$ orbitals (A sites).[6] Since the electron density near B sites is greater than that near A sites, non-bonded *d* electron–ligand repulsions will be greater for the former. This qualitative argument appears to hold for the cobalt and manganese complexes (keeping in mind the high standard deviations of the bond lengths in these structural determinations). It cannot be applied to the zinc complex, nor does it hold for $[Fe(NO_3)_4]^-$, isoelectronic with $[Mn(NO_3)_4]^{2-}$, where the Fe–O bonds are reported to be equal.[15] The suggestion that the equal bond lengths in $Ti(NO_3)_4$

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[10] S. J. Lippard and B. J. Russ, *Inorg. Chem.*, 1968, **7**, 1686.

[11] P. Cherin, W. C. Hamilton, and B. Post, *Acta Cryst.*, 1967, **23**, 455, and refs. therein.

[12] C. D. Garner, D. Sutton, and S. C. Wallwork, *J. Chem. Soc.* (*A*), 1967, 1949.

[13] C. D. Garner and S. C. Wallwork, *J. Chem. Soc.* (*A*), 1970, 3092.

[14] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 1963, **2**, 235.

[15] T. J. King, N. Logan, A. Morris, and S. C. Wallwork, *Chem. Comm.*, 1971, 554.

(ref. 16) and in $Sn(NO_3)_4$ (ref. 12) are related to the spherically symmetrical distribution of non-bonded metal *d*-electrons[15] is also inapplicable to the zinc complex. The other two effects, d_π–p_π bonding and ligand–ligand repulsions, are also difficult to apply in this case. The former is discounted since it again depends essentially on unequal *d*-orbital occupancy[17] and the latter[18] is ill adapted to correlating differences within closely related series such as that of Table 5.

The distortion from the ideal dodecahedron may be seen as tending to an elongated tetrahedron (*e.g.* Zn–O in ZnO is 2.10 Å,[19] close to the value for Zn–O_A). We conclude that the tendency to tetrahedral co-ordination of Zn^{2+} may be the major factor responsible for the difference between r_A and r_B.

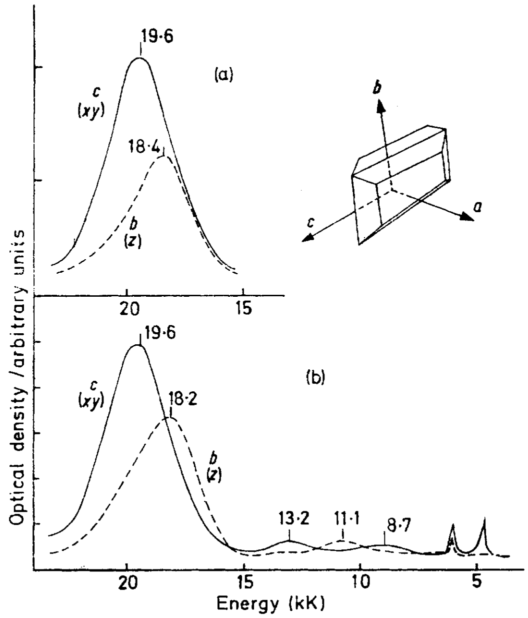

FIGURE 2 Optical spectra: (a) $[AsPh_4]_2[Co(NO_3)_4]$ (100) face with *E* parallel to *b* and *c*, visible region only, and (b) Co^{2+}/$[AsPh_4]_2[Zn(NO_3)_4]$, (100) face. The morphology of the Zn^{II} complex is shown in the inset

Crystal Spectra of $[Co(NO_3)_4]^{2-}$.—Figure 2 shows the visible and near-i.r. spectra of the cobalt-doped species, obtained with the electric vector, *E*, incident on the (100) face and parallel to *b* or *c*, together with that, in the visible region only, of the undiluted complex. For both cases, spectra of the (010) face showed little difference in absorption along *a* and *c'* (a direction orthogonal to the extinction direction *c*), these differences being no more than *ca.* 150 cm^{-1}. The *z* axis is defined as lying parallel to the crystallographic *b* axis (the C_2 molecular axes being aligned in the crystallographic *b* direction, the alignment is the same as that for the Mn^{II} analogue described in ref. 6). The *x* and *y* molecular axes are defined as lying between the M–O bonds (Figure 1). Since the spectrum of *a* is virtually identical to that of *c'*, all spectra perpendicular to *b* will be referred to as *xy* spectra and the misalignment between molecular axes *x* and *y* and crystallographic axes *a* and *c'* may be ignored.

The spectra consist of a relatively intense band at 19.6 kK with a very weak shoulder at lower energy, the latter being rather more marked in the pure compound, when *E* is parallel to *a* or *c'* (*i.e. xy*). When *E* is parallel to *b* (*i.e. z*) there is a single relatively intense band at 18.4 kK (18.2 kK in the dilute species). The near-i.r. region is less clear, but two broad bands may be discerned at 13.2 (*xy*) and 11.1 kK (*z*). There is a further, even weaker, band at *ca.* 8.7 kK (*xy*). Low-intensity narrow bands below 6 kK are vibrational in origin since they are also present in the free matrix. No further absorptions ascribable to *d*–*d* transitions were found at higher (<28 kK) or lower (>300 cm^{-1}, on an i.r. spectrophotometer) energies. Spectra obtained at liquid-nitrogen temperature were little different; the intensities of both bands in the visible region decreased slightly.

With the axis system as already defined above, the terms of Co^{2+} in T_d symmetry transform as: $^4T_1(F)$ and $^4T_1(P)$: $^4A_2 + {}^4E$; $^4T_2(F)$: $^4B_2 + {}^4E$, on descent in symmetry to D_{2d}, the ground state being $^4B_1$. The electric dipole selection rules are:

$$^4B_1 \rightarrow {}^4E \;\; xy \quad (xy\colon\; A_1 + A_2 + B_1 + B_2;\;\; z\colon\; E),$$

$$^4B_1 \rightarrow {}^4A_2 \;\; z \quad (xy\colon\; E;\;\; z\colon\; A_2),$$

$$^4B_1 \not\rightarrow {}^4B_2 \quad (xy;\; E;\;\; z\colon\; B_1).$$

Vibrations given in parentheses are those allowing possible vibronic transitions.

In the cobalt-doped matrix, the bands at 19.6, 13.2, and (less securely) 8.7 kK may be assigned to $^4E \leftarrow {}^4B_1$ transitions and those at 18.2 and 11.1 kK to $^4A_2 \leftarrow {}^4B_1$ transitions. In agreement with the simple electric-dipole selection rules, the $^4B_2 \leftarrow {}^4B_1$ transition cannot be located.

Thus, despite the very small differences between *x* and *y* directions, the spectra are better interpreted by the gross D_{2d} selection rules rather than by those for C_{2v} symmetry. Preliminary crystal-field calculations allow a rationalisation of this energy-level order.[20]

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